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INVESTIGATIONS ON CHLOROPHYLL

II.—SEPARATION OF CHLOROPHYLL *a* AND *b* BY CHROMATOGRAPHIC METHOD, USING UREA AS ADSORBENT

BY

Salar Masood, A. W. Siddiqi and M. Qureshi

INTRODUCTORY.—The Chlorophyll mixture ($a+b$) obtained from leaf powder by the methods described in a previous paper [1] can be separated into its components by two different methods :—

The method of Willstatter and Stoll [2] is based on the principle of the distribution of chlorophyll between petroleum ether and aqueous methyl alcohol. When a solution of the chlorophyll mixture in petroleum ether is extracted with 85 per cent. methyl alcohol, previously saturated with petroleum ether and acidified, immediately before use, with oxalic acid (0.01 gm. of oxalic acid per litre), the component *a* prefers the petroleum ether phase, while the component *b* accumulates in the methyl alcohol layer. The separation of the two components requires a number of extractions (14 to 16) and large quantities of solvents. The methyl alcoholic extracts are brought to a concentration of about 90 per cent. by the addition of methyl alcohol, washed thoroughly with petroleum ether, and extracted with ether. The ethereal layer is freed from methyl alcohol by washing with water. dried with anhydrous sodium sulphate and evaporated down to a small volume under reduced pressure. The addition of low-boiling petroleum ether to this solution leads to the precipitation of chlorophyll *b* which is filtered on talc, extracted with ether and purified by re-precipitation with low-boiling petroleum ether and re-extraction with ether. The petroleum ether solution, after extraction with methyl alcohol is washed with water till chlorophyll *a* is precipitated. The suspension is shaken with anhydrous sodium sulphate and talc and filtered through a layer of talc under weak suction. The pigment is extracted from the talc with ether and the ether is completely removed by evaporation in a vacuum desiccator. The yield in one of the experiments of Willstatter and Stoll amounted to 3.7 gm. of chlorophyll *a* and 1.15 gm. of chlorophyll *b*, from 8 gm. of the chlorophyll mixture with the component ratio 2.8, while 2.3 gm. of a chlorophyll mixture were recovered as a by-product.

The other method employed for the separation of the chlorophyll mixture into its components is the so-called 'chromatographic' method, (or chromatographic adsorption analysis), originated by Tswett [3] in 1906. This method, which has now received a much wider application through its successful use in the isolation of carotins and vitamins and in the analysis of colourless substances, is based on the fact that powders adsorb pigments as well as colourless substances to different extents from their solutions in organic solvents. The method consists in allowing the solution of the pigment in petroleum ether or any other suitable solvent to filter through a column of some suitable adsorbing powder, such as calcium carbonate, alumina, talc or cane-sugar. As the solution passes through the column its various components are adsorbed to different extents, defending upon their adsorption affinities. When the solution comes in contact with the topmost layer of the adsorbent, the component with the strongest affinity for the adsorbent is retained, while those with less affinities pass through and are deposited down below. The separation, at first, is not quite complete but as more of the solution passes through, the components with less adsorption affinities are gradually displaced by those possessing more adsorption affinities for the adsorbent and ultimately different components are deposited at different parts of the column giving rise to a number of coloured zones. The passage of the pure solvent through the column, afterwards, leads to a further differentiation of the zones or the 'development' of the "chromatogram."

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[1] Investigations on Chlorophyll, Part I—Qureshi and Srivastava, this Journal, Vol. VI, p. 1.

[2] Investigations on Chlorophyll by Willstatter and Stoll, p. 146.

[3] Ber. Bot. Gez. 24, 316, 384, 1906.

Winterstein and Stein [1] have employed Tswett's method for the separation of chlorophyll mixture into its components, using a mixture of cane-sugar and talc (6 : 1) as the adsorbent. According to these authors, cane-sugar is the most suitable adsorbent for the separation of chlorophyll pigments. The other powders used by Tswett, such as calcium carbonate, alumina and talc, were found unsuitable for the purpose, on account of the slight decomposition suffered by the pigments on their surfaces. Bakker [2] has also employed cane-sugar for the isolation of pigments from the extracts of leaves.

The object of the present investigation was to isolate the two chlorophylls from the extract of plant leaves, chromatographically, using urea as the adsorbent. As a result of the experiments, carried out by the authors, it has been found that powdered and dry urea mixed with talc in a certain proportion is a very suitable adsorbent for the separation of the principal pigments contained in the extract of plant leaves. Comparative experiments, carried out under the same condition with cane-sugar as the adsorbent, showed that a better differentiation of zones was obtained with urea than with sugar.

EXPERIMENTAL

Drying of leaves. - The plant leaves (*Cestrum Nocturnum*) were dried in a special wooden drying chamber constructed for the purpose. The chamber had several compartments with perforated bottoms on which leaves were spread out in single layers. The inside air was heated by means of electrically heated coils of wire placed at the bottom of the chamber and was kept circulating through the compartments with the help of an electric fan located at the top of the chamber and a system of conducting pipes. Fresh air, when required, could be drawn into the chamber through holes at the sides of the chamber near the bottom which could be closed or opened at will. The temperature of the chamber was controlled and kept constant between 38° and 40° by means of a regulator and an electric relay. The leaves were completely dry and ready for pulverisation after three days.

Extraction of pigments.--The procedure adopted for the extraction of pigments may be illustrated by the description of one experiment :—

100 grams of the leaf powder were soaked with petroleum ether (B.P. 70°-80° C) and left overnight. The next day, the petroleum ether was sucked out and the

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1. Zeitschr. Physiol. Chem. 220, 263, 1933.

2. Proc. Kon. Akad. Amsterdam, 37, 679, 1934.

material was treated successively with benzene and acetone and finally sucked dry. After this preliminary treatment, the leaf meal was extracted with 80 per cent. acetone, under moderate suction, until the material assumed a straw yellow colour. 500 c.c. of acetone were required for the extraction which took about 30 minutes to complete. The green acetone extract was then transferred into a 2-litre separating funnel, containing 200 c.c. of petroleum ether, in two portions. After the addition of each portion, the funnel was rotated slowly, 50 c.c. of water were added, and the yellowish green acetone layer removed. The petroleum ether solution was, now, washed thrice with 50 c.c. of 80 per cent. acetone and the layers removed on complete separation. The acetone was removed by six successive washings, using 25 c.c. of water each time. The object of these washings was to remove as much of acetone as was possible without the precipitation of the pigments. The petroleum ether solution, thus obtained, was dried by keeping it in contact with anhydrous sodium sulphate for an hour, filtered, and used for chromatographic adsorption analysis.

Separation of pigments.—As already mentioned, Winterstein and Stein tried different adsorbents and found that cane-sugar mixed with talc (6 : 1) was the most suitable adsorbent for the separation of chlorophyll components. The present authors carried out a number of experiments with sugar and urea in order to ascertain if the latter could be substituted for the former with some advantage. These preliminary tests revealed that under certain conditions urea behaved better as far as the differentiation of zones was concerned. The only difficulty in the case of urea was the lightness of its particles, which makes itself felt in the preparation of the adsorbing column. The particles take a long time to settle even under strong suction and the column suffers a continuous shrinkage during the experiment. This difficulty was overcome by mixing it with talc in the proportion of four to one. With this mixture a compact column can be obtained in a comparatively short time and this does not show any further shrinkage during the course of the experiment. After having discovered the best conditions of work, the main experiments were conducted as follows : –

Crystals of pure urea dried for half an hour at a temperature of 55° to 60° were powdered and passed through a sieve of 170 meshes per inch. The powder was further dried for two hours at 55°-60°, allowed to cool slowly in vacuum, and thoroughly mixed up with talc powder (4 : 1) of the same grade of fineness which had been dried at 80°. The adsorption apparatus consisted of a glass tubing 25 c.m. long and 2 c.m. wide. This was closed with a tight fitting cork and connected by means of a vertical glass tubing, carrying a stop-cock, with another tube below. The lower tube had a side-tube for connection with water pump. The bottom of the upper tube was covered with glass wool, nickel wire gauze and filter paper. The urea mixture made into a thin paste with petroleum ether (70°-80°), was introduced into the upper tube in portions, and suction applied after the addition of each portion. This was continued until the tube was nearly filled with the mixture. Care was taken to keep the surface covered with liquid during the whole operation. Petroleum ether was, then, sucked through the column several times until the particles settled down and there was no further shrinkage of the column. Similar procedure was adopted in experiments in which cane-sugar was employed as adsorbent. After the column was ready, the solution of chlorophyll pigments in petroleum ether prepared by the method described above was dropped over the surface of the column and allowed to diffuse downwards under moderate suction. This was followed by a small quantity of the pure solvent, which helped to differentiate the zones. The column was afterwards sucked dry. The operation resulted in the formation of three and occasionally four distinct zones in the following order counting downwards.

(*a*) a bright green zone containing mainly chlorophyll *b*
(*b*) a bluish green zone containing mainly chlorophyll *a*
(*c*) a yellowish zone containing xanthophyll and carotine, and
(*d*) a grey zone containing pheophytin.

The solid column of the adsorbent was carefully pushed out of the tube by means of a wooden rod and cut into different portions. The portions containing chlorophyll *a* and *b* were stirred and washed separately with an acetone-ether mixture (1 : 1) until the pigments were completely removed. The filtrate was transferred into a separating funnel and washed free of acetone by adding water. The ethereal layer, after being dried over anhydrous sodium sulphate, was evaporated down to dryness in a vacuum desiccator. Each pigment was further purified by repeating the process with a fresh column of the adsorbent. The average yields of the two pigments per 100 gm. of the leaf powder were as follows :—

Absorbent used	Chlorophyll *a* (gm.)	Chlorophyll *b* (gm.)
Urea ..	0.26	0.12
Cane-sugar ..	0.22	0.12

Purity tests carried out on the samples showed that the pigments had not suffered allomerisation and that the phytol group was intact. Some samples were found to contain a very small quantity of the yellow pigments.

STUDIES ON CHROMIUM HYDROXIDE SOLS

By

D. S. Datar and M. Qureshi

INTRODUCTION

In their investigation of the effect of sunlight on a number of sols, Miss Roy and Dhar (Jour. Phys. Chem. 1930, XXXIV, 122-37) found that in general the effect of light on sols is in the same direction as that of ageing and the light effect is much more pronounced than the time effect. Sols can be divided into two groups : – (1) those which become unstable towards electrolytes on exposure to light, and (2) those which become more stable. The coagulation of a sol by light is, according to them, mainly due to (1) the decomposition of the stabilising ion and (2) loss of reactivity of the sol particles and its consequent giving up of the adsorbed electrolyte. The chromium hydroxide sol becomes less stable towards electrolytes and shows an increase in electrical conductivity after exposure to light. S. Horiba and H. Baba (Jour. Phys. Chem. Japan 1929, 3, 1-15) have also come to a similar conclusion. G. H. Ayres (J. Amer. Chem. Soc., 1936, 58, 18-22) finds that heat treatment reduces the stability of the chromic oxide sol. No further work of a quantitative and systematic nature has been done on the subject. In the investigation described below an attempt has been made to make a thorough investigation of the effect of ultra-violet light on chromium hydroxide sols by studying simultaneously changes in extinction coefficients, pH values and conductivities.

EXPERIMENTAL

In all the experiments described below the dark green crystals of chromium chloride prepared by Merck were used for the preparation of different chromium hydroxide sols. Doubly distilled water and well-steamed and dry vessels of pyrex were used throughout the work. Extinction coefficients were measured in 10 cm. tubes with a Hilger Nutting Spectro-photometer. pH values were determined with a quinhydrone electrode connected to a saturated calomel electrodes, and potential difference was measured with a K type potentiometer of Northrup and Leeds. Conductivity measurements were made by the Kohlrausch bridge arrangement. The source of ultra-violet light was the immersion type quartz mercury vapour lamp run on 110 Volts D.C. and 2.5 amperes. To keep the temperature constant, the lamp was surrounded by a quartz jacket through which cold water was kept running. The jacket was immersed in a beaker containing the solution to be illuminated and the solution was stirred to ensure uniform illumination.

For the estimation of chromium and chlorine in chromium hydroxide sols the following procedure was adopted :—

Determination of Chromium.—To 20 c.c. of the solution 10 c.c. of concentrated hydrochloric acid and a few drops of methyl red (0.2 per cent. alcoholic solution) were added and the mixture heated just to boiling. Dilute ammonia was then added dropwise until the colour of the solution changed to a distinct yellow. It was boiled once again for two minutes and filtered at once. The precipitate, after being thoroughly washed with hot 2 per cent. ammonium chloride solution, was ignited in a platinum crucible and, after all carbon was burnt off, blasted for 5 minutes. The crucible was covered and kept in a vacuum desiccator and after it had cooled down was weighed as rapidly as possible. It was blasted again for 5 minutes and weighed rapidly and accurately.

Determination of Chlorine.—To 25 c.c. of the solution 10 c.c. of concentrated nitric acid and 5 c.c. of N/10 silver nitrate were added and the solution diluted to 75 c.c. It was heated for three hours at 60° C. when all the chromium hydroxide dissolved in nitric acid. Silver chloride was allowed to settle, filtered in a platinum gooch crucible and washed first with cold water acidified with nitric acid and then with cold water alone. It was dried for three hours at 130° C. and weighed. The drying was continued until constant weight was obtained.

Preparation and purification of Sols.—The following three methods were employed for preparing chromium hydroxide sols.

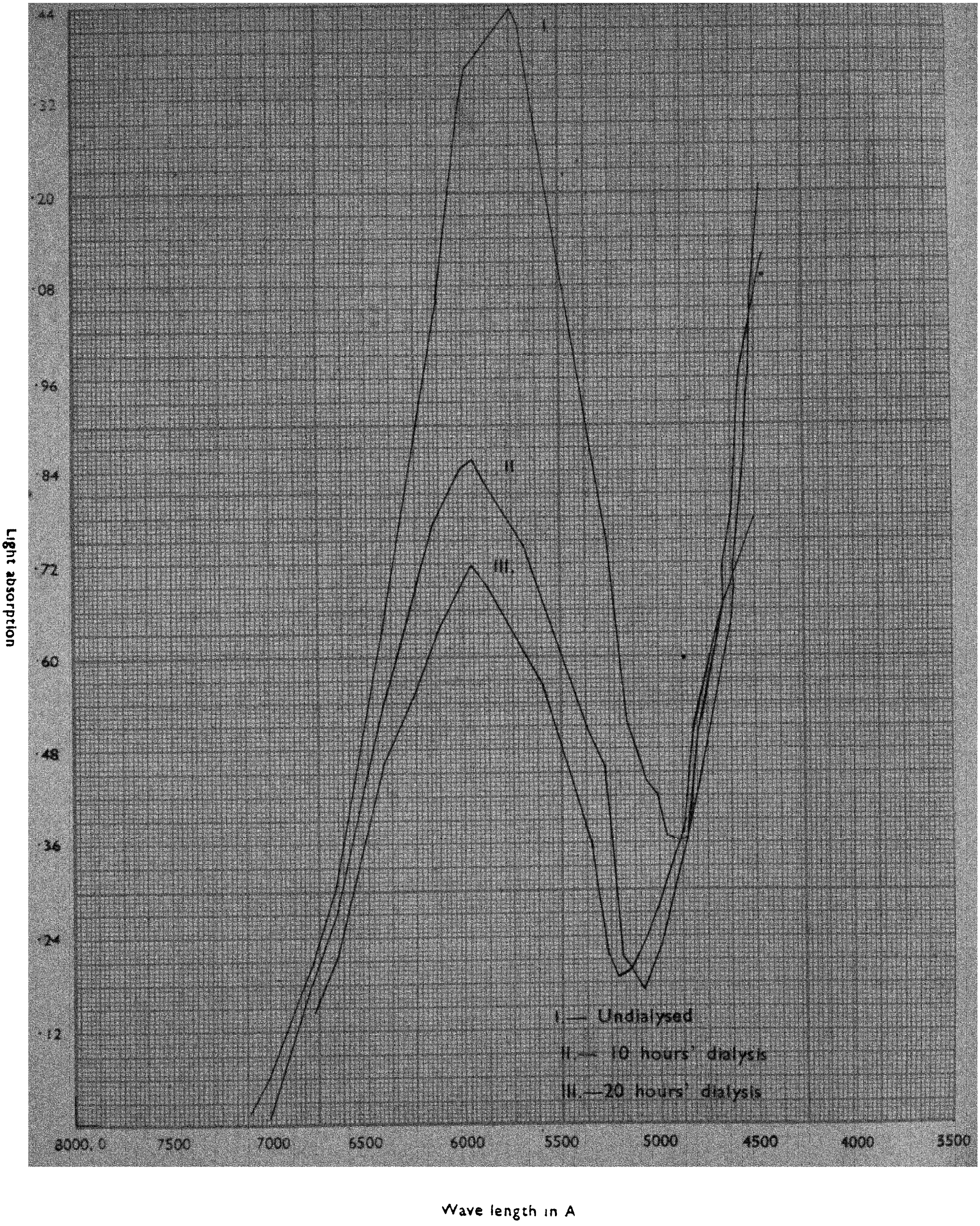
(*i*) Chromium hydroxide was precipitated by adding ammonia to a hot solution of chromium chloride. Half of the precipitate was dissolved in the least amount of 6N hydrochloric acid. More hydroxide was then added to the solution and the mixture allowed to peptonise into a thick solution. This solution, after addition of water, was filtered and dialysed by the process of continuous hot dialysis.

(*ii*) A molar solution of chromic chloride was made to fall at the rate of two drops per second into vigorously boiling distilled water. The solution was then dialysed.

(*iii*) 98 c.c. of normal ammonia were added to 324 c.c. of normal chromium chloride with vigorous shaking. After standing for 30 minutes, it was dialysed.

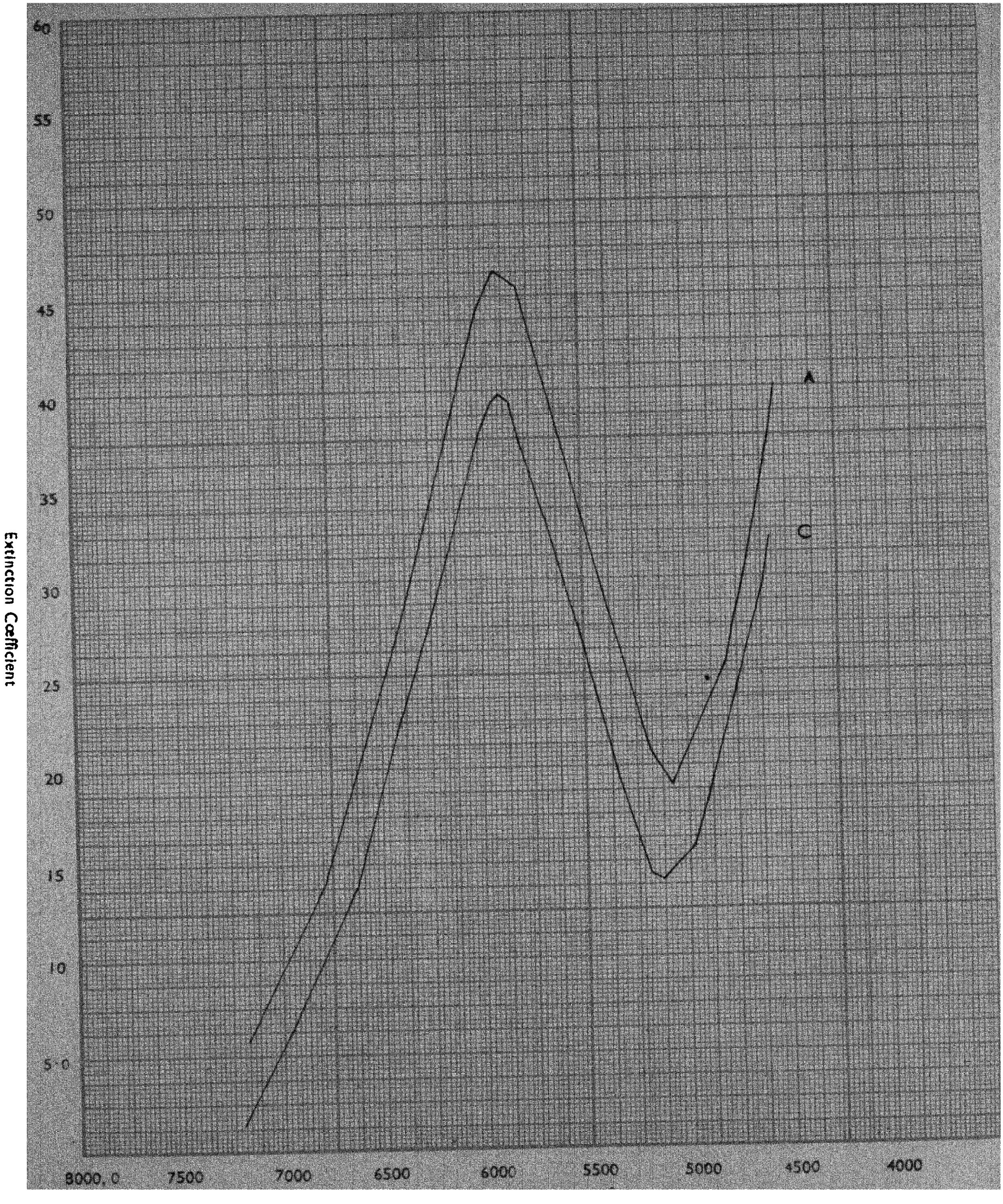
Neidle's method of continuous hot dialysis was employed for dialysing the sols. The temperature of dialysis was kept between 80°-95°C. It was observed that during the first stages of dialysis (for the first 10-15 hours) chromium hydroxide colloid diffused through the parchment membrane. The progress of dialysis was followed by performing the silver nitrate test on the diffusate and observing electrical conductivities of the colloidal solution. These observations in the case of one of the sols are given in Table I. As shown in the table, it was found that conductivity decreased and ultimately reached a value approaching that of distilled water (1.36×10^{-6}) after 70 hours dialysis. At this point the dialysis was stopped.

The progress of dialysis was also followed through observation of changes in the light absorption of the solution. Full absorption curves were determined for a sol prepared according to the method (2) given above. The dialysis of the sol was con-



Light absorption
·44
·32
·20
·08
·96
·84
·72
·60
·48
·36
·24
·12
8000, 0
7500
7000
6500
6000
5500
5000
4500
4000
3500
I
II
III.
I.— Undialysed
II.— 10 hours' dialysis
III.—20 hours' dialysis
Wave length in A

Fig I



Wave length in A

Fig. 2.

tinued up to 22 hours. The curves are shown in Figure I. The curves show a shifting of the region of maximum absorption towards the red.

TABLE I

Period of dialysis in hours	Specific conductivity	Silver Nitrate test with the diffusate
40	8.45×10^{-4}	Positive test
49	2.26×10^{-4}	do
55	8.68×10^{-5}	do
60	5.16×10^{-5}	Negative test
70	1.36×10^{-6}	do

Extinction coefficient curves of purified Sols. Two different sols (A and C Table II) were prepared by methods (*i*) and (*ii*) described above and dialysed for about sixty hours till their specific conductivities were nearly the same. Both were analysed for their chromium contents according to the method described above and the light absorption of the two sols at different wave lengths was determined with a Nutting Spectro-photometer. The results calculated as extinction coefficients according to the relation

$$E = \frac{1}{.DC} \log \frac{I_0}{I}$$

where C denotes the molar content of chromium oxide, have been plotted against wave-lengths in Figure 2. The two curves do not coincide, indicating a difference in size of particles.

pH values, specific conductivities and analytical data.– The characteristics of the different sols prepared by us, excluding the extinction coefficients data already given, are summarised in Table II.

TABLE II

Sols.	Method of preparation	Period of dialysis in hours	Concentration in Gram mol. of Cr_2O_3 per litre	pH value	Specific conductivity
A	1	60	.00503	5.91	3.25×10^{-5}
B	3	70	.00878	6.34	1.36×10^{-6}
C	2	57	.00422	5.62	4.16×10^{-5}

Effect of ultra-violet light.—Sol C, prepared by method 2 and dialysed for 57 hours was used for the study of the effect of ultra-violet light. A portion of this sol was illuminated by the method given above and its pH value and conductivity determined at different intervals of time. The results are recorded in Table III.

TABLE III

Period of exposure in hours	pH value	Specific conductivity
0	5.62	4.22×10^{-5}
6	5.61	5.64×10^{-5}
14	5.58	13.45×10^{-5}
24	5.68	6.42×10^{-5}

After 24 hours' exposure, the portion exposed to ultra-violet light and that kept in the dark were analysed for their chromium and chlorine contents by the methods described above. The results are given in Table IV. Marked decrease in the amount of total chlorine on exposure was observed.

TABLE IV

Period of exposure	Chromium in equivalents per litre	Chlorine in equivalents per litre	$\frac{\text{Chromium}}{\text{Chlorine}}$
0	.001371	.0004463	30.69
24	.001378	.000279	49.39

Extinction coefficients were measured for the exposed sol as well as for that kept in the dark. The values for different wave-lengths are recorded in Table V and the curves are shown in Figure 3.

TABLE V

Wave-length	Extinction coefficient for exposed sol.	Extinction coefficient for unexposed sol.
7210	1.51	2.06
6990	6.00	8.85
6640	13.84	18.15
6400	22.83	25.99
6230	29.23	35.63
5980	37.94	42.17
5940	38.72	43.11
5810	37.48	42.98
5660	33.46	41.02
5520	27.77	35.76
5340	19.45	29.30
5180	14.48	26.50
5110	15.35	25.28
4990	16.07	30.35
4860	18.31	32.92
4770	24.05	39.49
4640	29.89	51.65
4620	32.49	55.30

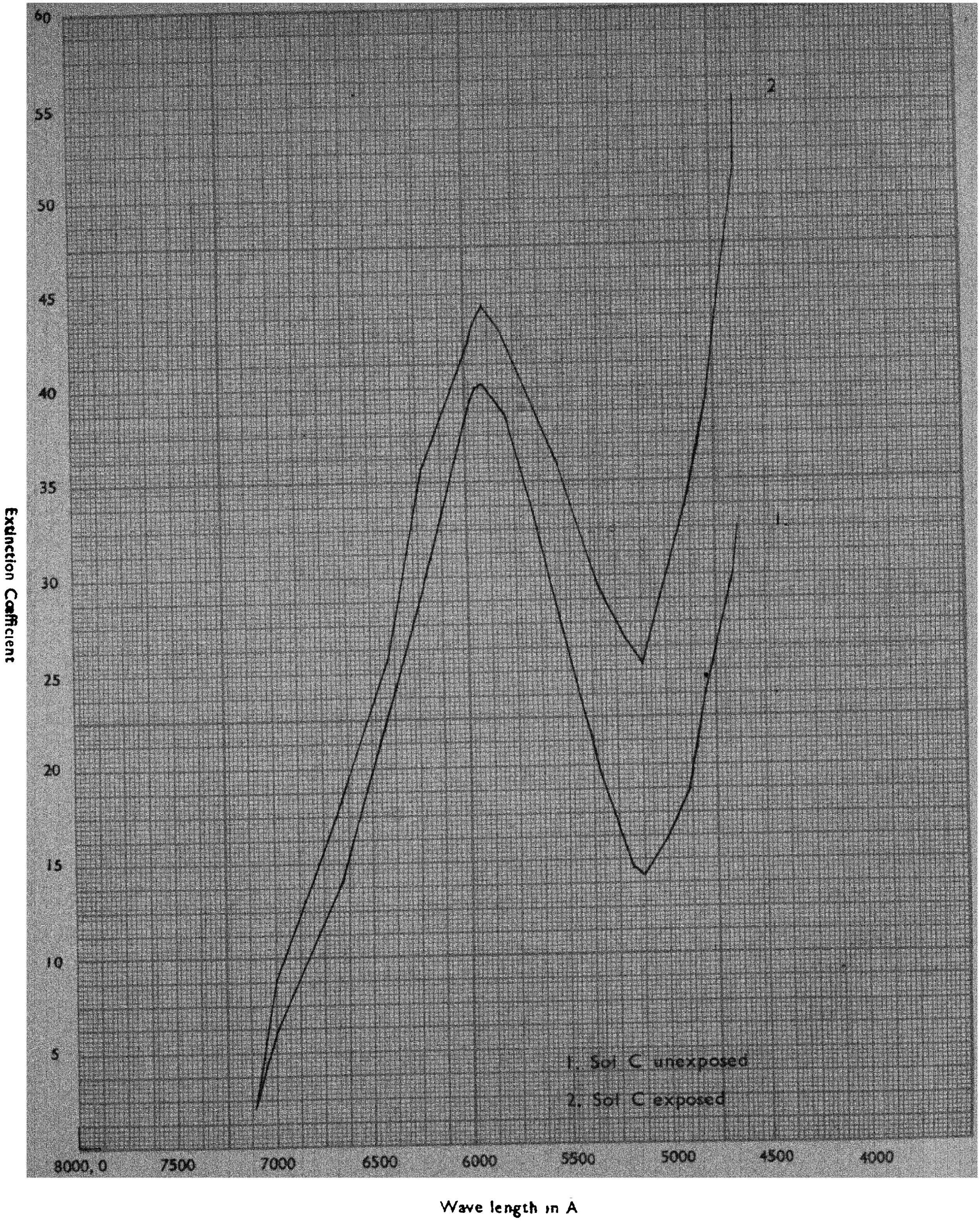

Extinction Coefficient
60
55
50
45
40
35
30
25
20
15
10
5
8000, 0
7500
7000
6500
6000
5500
5000
4500
4000
Wave length in A
2
1.
1. Sol C unexposed
2. Sol C exposed

Fig. 3.

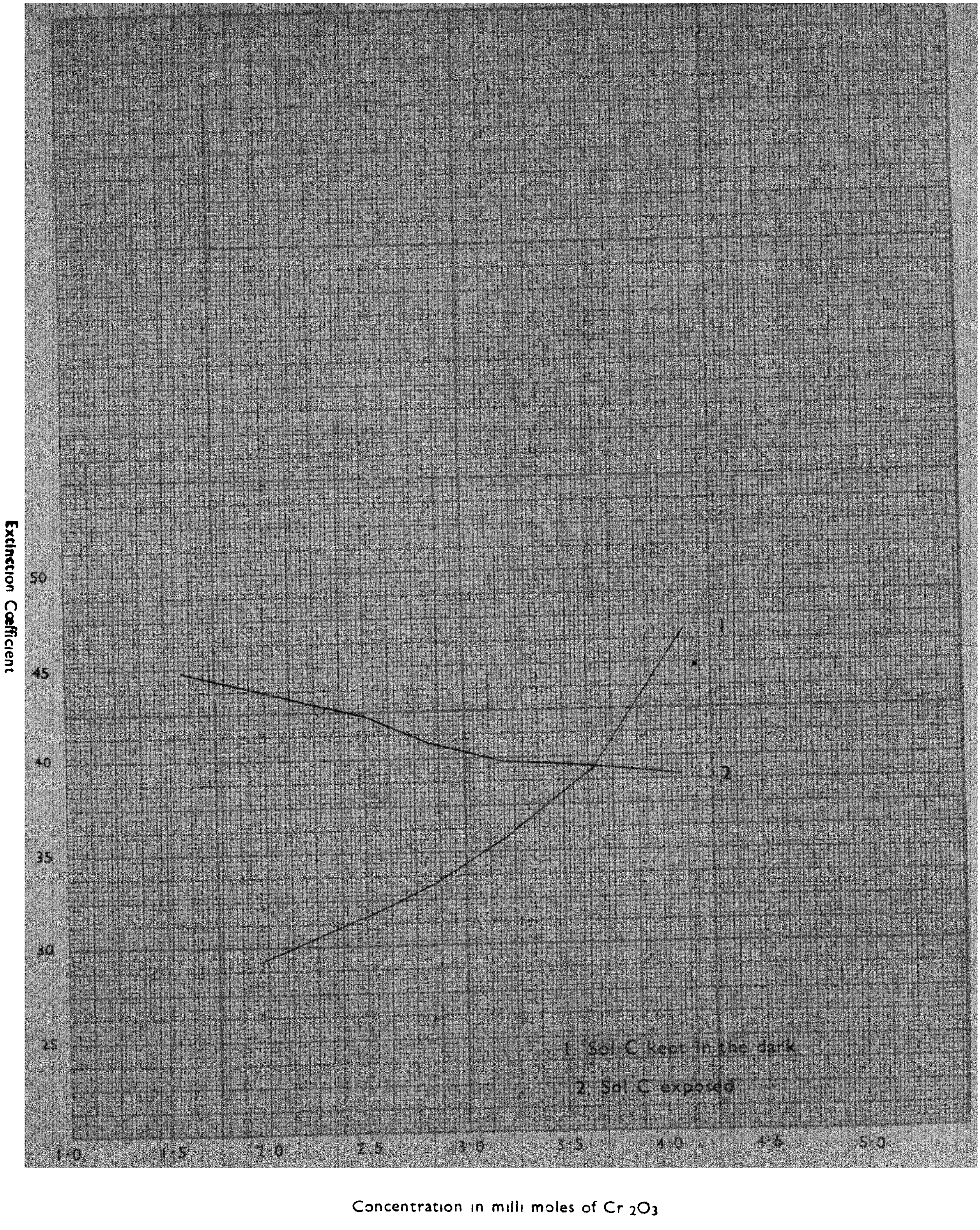

Extinction Coefficient
50
45
40
35
30
25
1·0,
1·5
2·0
2.5
3·0
3·5
4·0
4·5
5·0
1
2
1. Sol C kept in the dark
2. Sol C exposed
Concentration in milli moles of Cr_2O_3

Fig 4

Effect of dilution.—Two portions of the sol C, one kept in the dark and the other exposed to ultra-violet light for 24 hours were employed for the experiments. A portion of the sol was transferred to a 10 cm. tube and its extinction coefficient determined for a particular wave-length, *viz.*, 5940. It was then diluted by successive addition of 2 c.c. of conductivity water to 15 c.c. The results are tabulated in Table VI and illustrated graphically in Figure 4.

TABLE VI

SOLS KEPT IN THE DARK		EXPOSED SOLS	
Concentration (Moles per litre)	Extinction Coefficient	Concentration (Moles per litre)	Extinction Coefficient
0.004112	38.72	0.004125	46.59
.003628	39.28	.003640	39.06
.003203	39.57	.003212	35.55
.002806	40.69	.002890	33.29
.002494	42.18	.002550	31.60
.001559	44.70	.001985	29.11

The same sols were also employed for the study of changes in the pH value on dilution. On dilution the hydrogen ion concentration should diminish. The pH values of these sols diluted to one-half and one-fourth of their original concentration respectively were measured. These are given along with the calculated values in Table VII. The observed value in each case is less than the calculated value.

TABLE VII

Sol.	Concentration	pH value obs.	Concentration	pH value		Concentration	pH value	
				obs.	cal.		obs.	cal.
Unexposed ..	.004112	5.49	.002056	5.47	5.79	.001028	5.52	6.09
Exposed ..	.004125	5.33	.002062	5.35	5.63	.001031	5.38	5.98

Effect of ageing.—One of the dialysed sols (C) was stored in the dark and its pH value and conductivity determined at long intervals extending over many days. The results given in Table VIII show that its pH and conductivity attain constant values in about a month's time.

TABLE VIII

Period of Ageing		pH Value	Conductivity
Months	Days		
	0	5.62	4.16×10^{-5}
	13	5.61	4.22×10^{-5}
	27	5.59	5.01×10^{-5}
1	2	5.54	5.99×10^{-5}
1	11	5.54	5.99×10^{-5}
1	16	5.54	5.99×10^{-5}

SUMMARY AND DISCUSSION

(1) The dialysis of chromium hydroxide sols was followed through observation of light absorption and specific conductivity. Specific conductivity decreased with continuous dialysis until a value approaching that of distilled water was reached. The nature of the light absorption curve (Figure 1) of an undialysed sol is somewhat similar to that of the violet variety of the chromium chloride, the point of maximum absorption in both cases occurring at about 5750 A. On continued dialysis, however, this maximum point shows a tendency to shift towards the red.

(2) The complete extinction coefficient curves of two sols prepared by different methods and dialysed for about 60 hours are shown in Figure 2. The concentration of each sol was determined by chemical analysis after complete dialysis. The extinction coefficients for different wave-lengths of the visible spectrum were determined by means of a Hilger Nutting Spectro-photometer. The curves do not coincide, indicating a difference in the size of particles, but they have the same form and the same regions of maximum and minimum absorption. The point of maximum absorption or the peak of the curve, in both cases, lies at about 5900 A, while the region of minimum absorption is near 5150 Å, followed by a steep rise towards the violet up to 4500 Å. These curves may be taken as the characteristic absorption curves of pure chromium hydroxide sol.

(3) Exposure for 24 hours to ultra-violet light of a sol dialysed for about 60 hours results in an increase in light absorption (Figure 3). The pH value shows a decrease on short exposures and an increase on long ones. Similarly, conductivity first increases and then decreases. These effects of exposure to ultra-violet light taken together may be explained in the following way :-

Exposure to ultra-violet light increases the hydrolysis of chromium chloride, adsorbed on the colloidal micelle, leading to an increase in the size of particles due to increased adsorption of water. The increase in the size of particles is followed by an increase in light absorption, while the diffusion of HCl into the dispersion medium gives rise to a decrease in the pH value and a corresponding increase in conductivity. Prolonged exposure, however, leads to the destruction of HCl and this has the effect of increasing pH value and decreasing specific conductivity.

Dhar and Roy (loc. cit.) have attributed the action of light to the photochemical acceleration of the reactions taking place in the dark. Our results, however, show that though the effect of short exposure is in a way similar to that of ageing the colloids behave peculiarly on long exposure. Lal and Ganguli (J. Ind. Chem. Soc. 1929, 6, 54) suggested that the ultra-violet light disturbs the equilibrium between the chloride adsorbed and that in the dispersion medium through the decomposition of the HCl in the surrounding liquid. More electrolyte diffuses out of the micelle to establish the equilibrium, rendering the colloid less stable. Our results, however, show that the hydrogen ion concentration does not diminish continually as the above observation of Lal and Ganguli would require but increases in the beginning and then decreases.

(4) The effect of dilution on the extinction coefficient, of unexposed and exposed sols, as recorded in Table 6 and graphically illustrated in Figure 4, is very interesting. It is apparent from the figure that the extinction coefficient of the un-

exposed sol at a particular wave-length near the point of maximum absorption, *viz.*, 5940 Å increases on dilution, while that for the same sol exposed to ultra-violet light for 24 hours decreases considerably on dilution. The increase in the extinction coefficient in the first case may be partially due to an increase in the size of the particle on account of the hydrolysis of the adsorbed chromium chloride. The decrease in the second case is, however, difficult to explain on the same analogy. It is significant to note in this connection that the observed pH value in both cases is less than the calculated value for each dilution, indicating that in both cases the adsorbed chromium chloride is further hydrolysed.

(5) Ageing of the sol has been studied by observing its pH value and conductivity over long periods of time up to a month and a half. It is found that nearly constant values are obtained in about a month's time.

ELECTRO-DEPOSITION OF CHROMIUM FROM POTASSIUM DICHROMATE BATHS

PART IV.—IN PRESENCE OF FLUORIDE

BY

Srinivas Rao and S. Husain

The apparatus used was the same as mentioned in Part I, except that the glass vessel and the glass stirrer were covered with paraffin wax, the thermostat was set at 40° C. and the electrodes were placed 8 cms. apart.

Experiments were also performed on the throwing power of the bath at different current densities. For this purpose, a glass vessel (12 × 5 × 6 cms.) fitted with a glass stirrer, was taken. Anode was placed in the centre and two cathodes of the same size as anode were placed on either side of the anode.

The deposits obtained were examined microscopically and microphotographs were taken.

Results

TABLE No. I

Electrolyte : 0.5 M. $K_2Cr_2O_7$ +0.1 M. KHF_2

Serial No.	Current density amp./cm.^{2}	Time hrs.	Amount of Cu deposited in coulometer g.	Increase in wt. of cathode g.	Amount of Cr deposited g.	Current efficiency %	Nature of deposit
1	0.03	2	..	..	..	..	No deposit.
2	0.04	2	0.5541	0.0054	0.0053	3.5	On one side dull white uneven deposit.
3	,,	1	0.2789	0.0026	0.0024	3.0	do
4	,,	¾	0.2057	0.0019	0.0018	3.2	do
5	,,	½	0.1334	0.0011	0.0011	2.9	do
6	,,	¼	0.0712	0.0006	0.0005	3.7	Uniform dull deposit.
7	0.05	2	0.7684	0.0073	0.0073	3.47	On both sides dull white deposit.
8	,,	1	0.3764	0.0053	0.0053	5.1	One side uniform white.
9	,,	¾	0.2406	0.0034	0.0031	4.6	do
10	,,	½	0.1582	0.0020	0.0020	4.6	do
11	,,	¼	0.0852	0.0009	0.0008	3.4	do
12	0.06	1	0.3846	0.0056	0.0055	5.2	Half shining white and half dull white.
13	,,	¾	0.3085	0.0043	0.0042	5.1	do
14	,,	½	0.2012	0.0032	0.0032	5.8	do
15	,,	¼	0.1044	0.0014	0.0014	5.0	do
16	0.07	1	0.4733	0.0040	0.0039	3.0	Edges black.
17	,,	¾	0.3205	0.0034	0.0033	3.7	Upper edge white.
18	,,	½	0.2425	0.0027	0.0025	3.7	Dull white.
19	,,	¼	0.1298	0.0013	0.0012	3.4	do
20	0.1	1	0.7084	0.0065	0.0060	3.0	Uniform black deposit.
21	,,	¾	0.5135	0.0051	0.0047	3.4	do
22	,,	½	0.3285	0.0032	0.0029	3.2	do
28	,,	¼	0.1760	0.0019	0.0016	3.5	do

TABLE No. II

Electrolyte : 0.5 M. $K_2Cr_2O_7$ +0.15 M. KHF_2

Serial No.	Current density amp./cm.^{2}	Time hrs.	Amount of Cu deposited in coulometer g.	Increase in wt. of cathode g.	Amount of Cr deposited g.	Current efficiency %	Nature of deposit
1	0.04	1	0.2634	0.0020	0.0020	2.8	Very thin deposit on edges only.
2	0.05	2	0.6908	0.0054	0.0082	4.3	Uniform dull white deposit.
3	,,	1	0.3468	0.0038	0.0036	3.9	do
4	,,	¾	0.2718	0.0030	0.0030	4.0	do
5	,,	½	0.1740	0.0018	..	..	Loose flakes, uneven deposit.
6	,,	¼	0.0810	0.0006	..	..	do
7	0.06	2	0.8558	0.0140	0.0138	5.9	Black and white, uneven.
8	,,	1	0.4268	0.0066	0.0065	5.6	do
9	,,	¾	0.2848	0.0043	0.0040	5.1	Dull white uniform.
10	,,	½	0.2000	0.0028	0.0028	5.1	do
11	,,	¼	0.0972	0.0016	0.0016	6.0	Thin dull white deposit.
12	0.07	1	0.5148	0.0086	0.0082	5.8	Black, mixed with white, uneven.
13	0.08	1	0.6188	0.0102	0.0100	5.9	On both sides black mixed with white.
14	0.09	1	0.6202	0.0108	0.0105	6.1	do
15	0.10	1	0.6882	0.0112	0.0108	5.7	More black and white.
16	0.15	1	1.0341	0.0082	0.0074	2.6	Frosty deposit.

TABLE No. III

Electrolyte : 0.5 M. $K_2Cr_2O_7$ +0.2 M. KHF_2

Serial No.	Current density amp./cm.^{2}	Time hrs.	Amount of Cu deposited in coulometer g.	Increase in wt. of cathode g.	Amount of Cr deposited g.	Current efficiency %	Nature of deposit
1	0.05	2	0.6100	0.0036	0.0034	2.0	Very thin uniform deposit.
2	0.06	2	0.6668	0.0094	0.0093	5.1	Uniform white deposit.
3	,,	1	0.3522	0.0053	0.0052	5.4	do
4	,,	¾	0.2712	0.0036	0.0036	4.9	do
5	0.07	2	0.7694	0.0108	0.0105	5.0	do
6	,,	1	0.4168	0.0068	0.0062	5.4	do
7	,,	¾	0.2980	0.0040	0.0036	4.4	do
8	,,	½	0.1980	0.0016	0.0016	3.0	do
9	,,	¼	0.0992	0.0008	0.0008	3.0	Deposit on edges only.
10	0.08	1	0.4881	0.0075	0.0069	5.2	Uniform dull white.
11	0.09	1	0.5412	0.0090	0.0082	5.4	Black and white deposit.
12	0.10	1	0.6042	0.0110	0.0100	6.0	do
13	0.11	1	0.7012	0.0108	0.0101	5.3	Black mixed with white deposit.

TABLE IV

Electrolyte : 0.5 M. $K_2Cr_2O_7$ + 0.25 M. KHF_2

Serial No.	Current density amp./cm.^{2}	Time hrs.	Amount of Cu deposited in coulometer g.	Increase in wt. of cathode g.	Amount of Cr deposited g.	Current efficiency %	Nature of deposit
1	0.06	2	0 8398	0.0140	0.0138	6.0	White loose flakes.
2	0.07	2	0 9824	0.0218	0.0214	7 7	Uniform, bright lustrous and tenacious deposit.
3	,,	1	0.4756	0.0094	0.0094	7.2	do
4	,,	¾	0.8577	0.0068	0.0060	6.2	do
5	,,	½	0.2548	0.0086	0.0036	5.2	do
6	,,	¼	0.1546	0.0025	0.0022	5.2	do
7	0.08	2	1.2008	0.0240	0.0237	7 2	do
8	0.08	1	0.5524	0 0055	0.0054	3 6	do
9	,,	½	0.2658	0.0036	0.0035	4.7	do
10	,,	¾	0.4364	0.0057	0.0051	4.4	do
11	,,	¼	0.1444	0.0015	0.0015	4 7	do
12	0.09	1	0 6175	0.0079	0 0078	4.1	Bright, white shining and lustrous with a black tinge on edges
13	,,	¾	0.4964	0.0067	0.0066	4.2	do
14	,,	½	0.3072	0.0042	0.0038	4.5	do
15	,,	¼	0.1602	0.0016	0.0014	3 2	do
16	0.10	1	0.7096	0.0110	0.0102	5.3	Black and white, uneven.
17	,,	¾	0.5302	0.0108	0.0106	7.0	do
18	,,	¼	0.2058	0.0026	0.0022	3.9	do

TABLE No. V

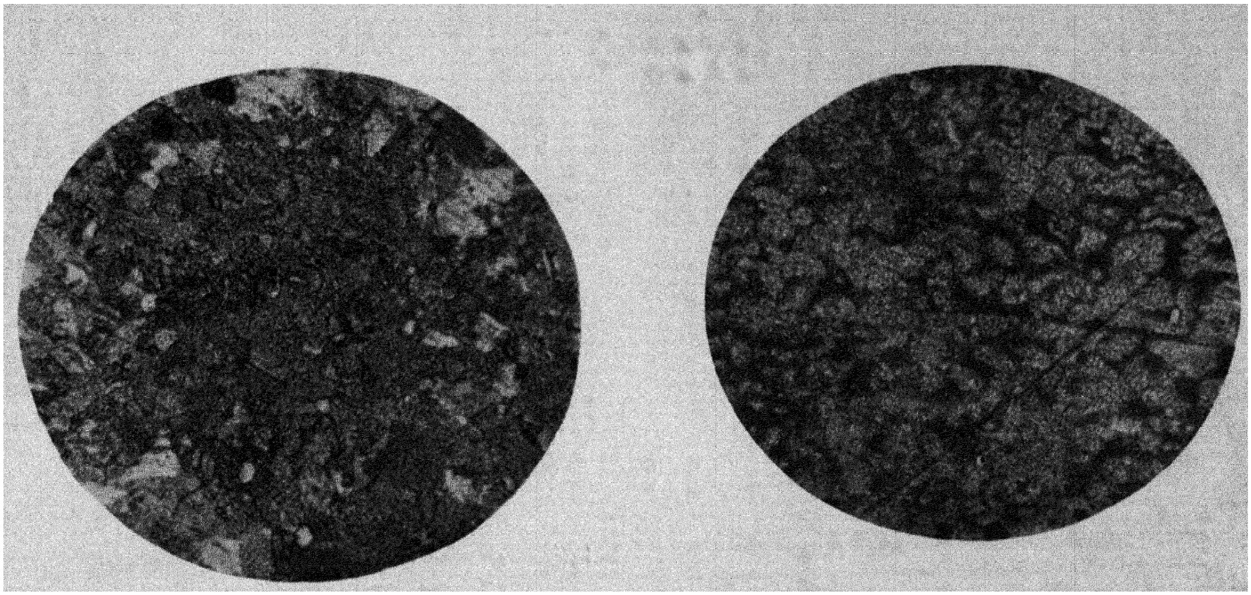
THROWING POWER

Electrolyte : 0.5 M.$K_2Cr_2O_7$ + 0.25 M. KHF_2, *Temperature* : 40° C., *Anode* : *Platinum*

No.	Current density amp./cm.^{2}	Time hrs.	Distance of cathode No. I from anode cms.	Distance of cathode No. II from anode cms.	Increase in wt. of cathode No. I g.	Increase in wt. of cathode No. II g.	P.C.D.R	Throwing power %
1	0.06	1	2	8	0.0035	..	4	—100
2	,,	1	2	6	0.0026	..	3	—100
3	,,	1	3	6	0.0025	..	2	—100
4	0.07	1	2	6	0.0040	..	3	—100
5	,,	1½	2	8	0.0069	..	4	—100
6	0.08	1	2	8	0.0079	..	4	—100
7	,,	1	2	6	0.0084	..	3	—100
8	0 09	1	2	8	0.0094	..	4	—100
9	,,	1	2	6	0.0098	..	3	—100
10	,,	1	3	6	0.0106	..	2	—100

Note.—**P.C.D.R. = Primary Current Distribution Ratio.**

As no deposit appeared on the distant cathode it was concluded that the throwing power was —100 per cent.



c. d. : 0·07 amp/cm²

0·08 amp/cm²

CONCLUSIONS

1. Potassium dichromate baths containing potassium hydrogen fluoride deposit chromium on electrolysis. Thus a bath containing 0.5 M. $K_2Cr_2O_7$+0.25 M. KHF_2 produces a bright lustrous and uniform deposit of chromium when electrolysed at a current density of 0.07 to 0.09 amp. /cm.^{2} with a current efficiency of 4 to 7 per cent.

2. The throwing power of the bath containing 0.5 M. $K_2Cr_2O_7$+0.25 M. KHF_2 is 100 per cent.

3. Microphotographs show that the deposits consist of crystals of chromium free from any impurities. Large crystals are obtained at low current densities, while those deposited at high current densities are fine and well-shaped.

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1. Journal of the Osmania University, 1935, III, 9.

SURFACE TENSION OF DIFFERENT DILUTIONS OF BOYS' SOAP SOLUTION

BY

N. Ramlal & S. Bashiruddin Nizami

INTRODUCTION

IN 1878 Professor W. Gibbs[1] showed that within a very wide limit the surface tension of soap solutions as determined by capillary tube is almost independent of strength. In 1890 Lord Rayleigh[2] proved that the surface tension of soap solutions changes with the freshness of the surface. In 1920 White and Marsden[3] determined the surface tension of various soap solutions and their emulsifying powers and found that, unlike the solution of sodium hydrate and many other salts, in soap solutions surface tension diminishes as concentration is increased. In 1922 Narayan and Subramanyam[4] using buble method showed that the surface tension of soap Solutions is the same for all concentrations between very wide limits.

In 1931 Mahajan[5] used weighing method for determining the effect of concentration on the surface tension of Boys' Soap Solution (2.5 per cent. sodium oleate and 25 per cent. Glycerine). He showed that the surface tension falls very rapidly as the amount of Boys' Soap Solution added to water is increased from zero to five per cent. From five to fifteen it falls slowly; after fifteen per cent. further addition of Boys' Soap Solution increases the surface tension instead of decreasing it, but this increase is very slow.

It was considered desirable to study the variation of the surface tension of Boys' Soap Solution by a dynamic method. Hence the ripples method was used.

METHOD

Experimental arrangements provided for the production of plane waves of known frequency and these were viewed in the intermittent light of double the frequency of the vibrator producing the ripples. The intermittent current maintaining the electrical tuning fork was passed through two small electro-magnets, each of which actuated a reed vibrator. One vibrator was used to produce ripples. It carried a glass microscope slide at its extremity, with its largest dimension horizontal. The

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1. Gibbs W., *Connecticut.* Acad. Trans. Part 2 (1877-88).
2. Rayleigh Lord *P. R. S.* XLVII, 127 (1890).
3. White and Marsden *Jr. Phys.* Chem. 24, 617 (1920).
4. Narayan and Subramanyam *Phil. Mag.*, 43. 663 (1922).
5. Mahajan and *Phil. Mag.* 272 (1931).

lower edge of the glass plate was made just to touch the surface of the liquid, which was contained in a developing dish. The lower portion of the glass plate was soaked well in chromic acid and then washed in tap water.

The other reed carried an aluminium plate with a slit cut out in it which passed in front of a similar fixed slit, as the reed vibrated. Both reeds were tuned to the frequency of the controlling fork.

A precision travelling microscope stood on a firm wooden bridge above the developing dish so that it travelled horizontally and parallel to the direction of propagation of the ripples. This microscope was fitted with a low power objective of such a focal length that it could be focused on planes above and below the surface of the liquid. A microscope cover slip was fitted over the objective at an angle of 45° to the microscope axis.

A horizontal beam of light from a pointolite lamp was directed on the slits and the intermittent emergent beam was rendered parallel by a convex lens. This beam fell on the 45° microscope cover slip, was reflected on the surface of the liquid and thence up to the microscope. The field of the microscope was seen to be crossed by a series of bright lines. These were due to reflection from the waves, both the crests and the troughs acting as cylindrical mirrors. The distance between two consecutive bright lines is $\frac{\lambda}{2}$ since the frequency of light is double that of the waves. The cross wires of the microscope were set on successive bright lines beginning at a point about 4 cm. from the dipper and moving away from it. During the process the microscope needed to be focused owing to the decreasing amplitude of the ripples. The surface tension was determined from the following:—

$$T = \frac{\lambda^2 p}{4\pi^2}(2n^2\pi\ \lambda - g)$$ where

T = surface tension
λ = wave length
n = frequency of reed
p = density of the liquid.

The Boys' Soap Solution was prepared in stock and kept in a cool dark place. By mixing different quantities of the same with water fresh solutions of different dilutions were prepared. Before each series of readings, the tray, the glass plate and the thermometer were washed with tap water, alcoholic solution of caustic potash, with chromic acid and with tap water again. The temperature of the liquid was kept constant by keeping the tray in a larger one containing water to which ice or hot water could be added to maintain the temperature constant.

RESULTS

Table I shows the values of surface tensions for different concentrations.

TABLE I

(*Temp.* 21° *C.*)

No.	Concentration	Surface tension	No.	Concentration	Surface tension
1	0 per cent.	74.31	9	40 ,,	29.90
2	3 ,,	39.80	10	50 ,,	30.83
3	4 ,,	31.41	11	60 ,,	31.50
4	5 ,,	30.18	12	70 ,,	31.97
5	10 ,,	28.21	13	80 ,,	32.38
6	15 ,,	27.21	14	90 ,,	32.80
7	20 ,,	27.48	15	100 ,,	33.02
8	30 ,,	28.85			

The results in table I are plotted with surface tensions as ordinates and concentrations as abscissæ. The part AB of the curve shows that the greater the concentration the less is the surface tension and the surface tension falls very rapidly as the concentration is increased from zero to five per cent. The part BC shows that the greater the concentration the greater is the surface tension, but this increase is very slow. This curve is similar to that obtained by Mahajan and thus confirms his results.

DISCUSSION

Mahajan has explained this marked minimum in surface tention thus—" It occurs only when the quantity of sodium oleate in the dilution is just sufficient to form a monolayer of particles on the surface of water. When the quantity of sodium oleate is greater than that required to form a monolayer the surface tension increases with the concentration of sodium oleate......"

The surface tension of soaps has been very extensively studied, but for the most part the results found in the literature are discordant, far beyond the experimental error. In general the surface tension diminishes rapidly with increasing concentration, reaching a steady or nearly steady low value, after a certain concentration is reached. The variation between the results obtained by different experimenters may be explained by hydrolysis of the soaps. Powney's recent observation gives a clue to the effect of hydrolysis. It does not seem possible as yet to explain these phenomena fully.

INVESTIGATIONS ON PALM JUICE

PART I.—ANALYSIS OF THE FRESH AND FERMENTED JUICE

BY

V. S. Basrur & M. Qureshi.

INTRODUCTORY

The palm trees, growing wildly over a vast area in Southern India, including the Hyderabad Dominions and the Provinces of Bombay, Madras and Bengal, are of a considerable economic importance to these parts of the country on account of the saccharine juice yielded by them on tapping. There are two different kinds of these trees, namely, the date palm (*Phœnix sylvestris* Roxb.), locally known as 'sendhi' and the palmyra palm (*Borassus flabellifer* Linn), locally known as ' toddy ' or ' tar.' Both of these varieties are found in the Hyderabad Dominions, but the date palm or sendhi trees are generally preferred for purposes of tapping, presumably because of their smaller height and comparative ease in tapping them. The tapping operation with the sendhi tree consists in making a V-shaped cut in the stem of the tree below the leaves and collecting the juice in an earthenware pot. The cut is made deeper and deeper on every alternate day for a period of about four months, after which the tree is given complete rest for two years. The tapping of the toddy palm is carried out by cutting off the flowers as they come up and collecting the exuded juice until the flowers are exhausted. The tapping is started in the evening and the pots are taken down from the trees in the morning, usually before sunrise. The total number of palm trees tapped in Hyderabad in the year 1937 A.D. according to the report of the Excise Department, was 2,57,678, of which 35,769, were the date palm trees, and the total revenue derived by the State from this source amounted to Rs. 1,17,47,308 in the Osmania currency, which is equivalent to Rs. 1,00,69,121 in the British Indian currency. This excludes the revenue from the trees on the Crown-lands which amounted to Rs. 3.71,109 in the Osmania currency for the year 1937.

The fresh palm juice, known locally as ' nira,' contains for the most part, cane-sugar, whose amount varies from 8 to 13 per cent. according to the nature of the tree, the time of the year and the method of tapping. The juice of the toddy palm is usually richer in sugar than that of the sendhi tree. The other important constituents present in the fresh juice in small amounts are reducing sugars (lævulose and dextrose), alcohol, glycerol, volatile acids (acetic acid), fixed acids (tartaric acid), starch, nitrogenous bodies (proteins) and mineral substances. Besides, the juice, as usually collected and brought down from the tree, is always found infected with yeasts and bacteria derived from the surface of the tree and the air. These vegetable micro-organisms multiply rapidly and bring about alcoholic and acidic fermentation which leads to the formation of alcohol, acetic acid, lactic acid, butyric acid and several other products in varying amounts depending upon the nature of the organisms present in the liquid and the conditions under which the fermentation is allowed to continue. When no special precautions are taken in the tapping of the trees and in the collection, transport and storage of the liquid, the spontaneous fermentation of the juice produces about 3 per cent. of alcohol and 0.1 per cent. of acids in the first 6 to 8 hours. After this the amount of alcohol first increases up to about 5 per cent. and then drops down gradually, while the amount of acids continues to increase, rendering the liquid unsuitable for human consumption. Butyric acid which is one of the many products of this spontaneous fermentation lends a disagreeable odour to the liquid, resembling that of the putrid butter or milk. The fermented liquid assumes a turbid appearance due to colloidal starch and suspended yeast cells, which gradually settle down as a yellowish-white deposit.

The palm juice, after it has undergone spontaneous fermentation for about 8 to 10 hours, is a common alcoholic beverage in these parts of the country which is consumed in large quantities everyday by the poor and labouring classes. The juice rendered sour on prolonged fermentation is usually thrown away, only limited amounts being employed for the preparation of vinegar. The conversion of the surplus alcoholic liquor into vinegar is carried out on a small scale by a primitive process which consists in simply leaving the liquid in a damp place for a long period of time. The juice, before fermentation, is valuable for its nutritive properties and vitamin content and is taken by some people as a morning drink. For this purpose the fresh juice or ' nira ' is collected in a new or disinfected pot and care is taken to keep the tapped surface thoroughly clean. The unfermented juice also serves as a source of crude sugar or ' jaggery ' and palm-sugar manufacture still exists as a cottage industry in some parts of the country. Mr. S. R. Bhate,[1] who made a study of the palm-sugar industry in Bengal, Bombay, Madras and Hyderabad in 1924, came to the conclusion that palm sugar industry developed as a cottage industry could well stand comparison with the sugar-cane industry. But taking into consideration the present position of the sugar-cane industry it is doubtful whether palm sugar can compete with its rival in the open market. It should, however, be possible, to use palm sugar for the preparation of some other articles of food such as sweatmeats, for which purpose this sugar seems to be better suited on account of its comparative richness in organic acids and proteins.

It is rather surprising that very little attention has been paid to the scientific study of the problems connected with the palm juice industries. After the useful work carried out by M. Damodaran[2] at the Institute of Science, Bangalore, in 1927, no serious attempt has been made, so far as the authors are aware, to study the organisms responsible for the fermentation of the juice and the products formed under natural and carefully controlled conditions. The chemical composition of the juice is also not known with certainty and much speculation is rife as to the amounts of certain substances, found to be present in the fresh and fermented liquid.

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[1] Bulletin No. 7 of the Industrial Laboratory, Hyderabad.

[2] Journal of the Indian Institute of Science, Vol. 11 A, Part VI, pp. 63-74.

It is obvious that fuller and more exact information on these points is needed before any steps could be taken to bring about any effective improvement in the existing palm juice industries or to employ the juice for purposes other than those for which it is being employed at present. Some years ago, investigations on palm juice were started in this laboratory with the above-mentioned objects in view, and as a first step many samples of the fresh juice, collected in disinfected glass vessels and earthenware pots from different trees and at different times of the year, were analysed both qualitatively and quantitatively. This work had to be suspended for some time, owing to the pressure of other work; but it was resumed last year and is now being continued. The present paper gives an account of the analytical work carried out on a large number of samples before and after fermentation. This will be followed shortly by other papers dealing with alcoholic and acetic fermentation under controlled conditions.

EXPERIMENTAL

The samples used in the analytical work described below were collected in disinfected glass vessels or earthen pots by a special arrangement with the tapper and under the personal supervision of a servant of the laboratory. On some occasions, the juice was supplied by the Excise Department who took special precautions to have the juice collected in new and disinfected vessels under the supervision of their own officials. The pots were tied to the trees in the evening and removed the next morning before sunrise. The juice was received in the laboratory before 7 a.m. and immediately placed in a refrigerator and analysed. About 30 samples from different trees were analysed at different times over a period of three years. The analytical work consisted in (*a*) the identification and estimation of the constituents of the fresh juice, (*b*) the identification and estimation of the constituents of the fermented juice and (*c*) the estimation of the sugar, alcohol and acid contents of the juice during the progress of fermentation. The methods employed for various tests and estimations were selected from (1) Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, (2) Allen's Commercial Organic Analysis, 5th Edition, (3) Villavecchia's Applied Analytical Chemistry (1918), and (4) Mulliken's Identification of Pure Organic Compounds. In the references quoted below, the first book is indicated by the abbreviation ' Official. '

A.—Analysis of the Fresh Juice

The following substances were tested and found to be present :—

1. *Sucrose* (cane-sugar) can be obtained in the form of crystals.
2. *Reducing sugars* (lævulose and dextrose) by their action on Pavy's solution.
3. *Ethyl alcohol* by the usual tests with the distillate from neutralised juice.
4. *Acetic acid* (in small quantities) by the usual tests with the steam distillate.

5. *Acetone* in traces. A light pink coloration was obtained in Legal's test performed with the distillate from neutralised juice.

6. *Tartaric acid.* It was precipitated as cream of tartar, which was tested by Denige's method with concentrated sulphuric acid and resorcinol.

7. *Glycerol* was identified in the syrup left on the evaporation of the fresh juice. The syrup, on being heated with a few crystals of potassium bisulphate evolved acrolein which was recognised by its smell. A strip of paper dipped in concentrated sodium nitroprusside solution containing a little piperidine was coloured deep blue.

8. *Nitrogenous substances* (proteins) were identified by Kjeldahl's method.

9. *Phosphate* was identified in the ash, obtained by the ignition of the evaporated juice, by the usual molybdate reaction and also by spot test.

10. *Carbonate* was identified in the ash.

11. *Sodium, Potassium and Calcium* were identified in the ash by spectroscopic examination and micro-tests.

The following compounds were tested in a number of samples and found absent in the fresh juice :—

1. *Formaldehyde.* Various tests performed with the fresh juice and its distillate (Official. p. 132. 18-24) gave no indication of formaldehyde.

2. *Acetaldehyde* was tested in the distillate obtained from the neutralised juice by the usual tests and found absent.

3. *Furfural.* 10. c.c. of the fresh juice or the neutralised distillate were shaken with 10 c.c. of concentrated acetic acid and allowed to stand. Absence of red coloration showed that furfural was not present.

4. *Butyric acid* was tested in the neutralised steam distillate of the juice and found absent.

5. *Lactic acid* was tested by Thoms' method and Uffelmann's reaction (Allen's Vol. I p. 769) and found absent.

6. *Malic, oxalic, citric* and *succinic* acids were tested in the syrup obtained by evaporating the juice on a water-bath, according to the methods given in Allen's Commercial Organic Analysis Vol. I.1924. and found absent.

7. *Magnesium* and *iron* were looked for in the ash and found absent.

8. *Sulphate* and *chloride* were tested in the residue obtained on evaporating the juice to dryness on water-bath and found absent.

The quantitative part of the work consisted in the estimation of the following in a number of samples :—Reducing sugar, total sugar, total acid, volatile acid, alcohol, total extract, glycerol, ash, phosphorus pentoxide and nitrogen.

The procedure adopted in each case was as follows :—

Reducing sugar.

A sample was exactly neutralised, clarified and titrated against Pavy's solution. The result is expressed as grams of invert sugar per 100 c.c. of the juice.

Total sugar.

25 c.c. of the clarified sample were heated with 2.5 c.c. of concentrated hydrochloric acid on a water-bath for half an hour. After rapidly cooling and neutralising the solution with sodium carbonate, it was made up to 100 c.c. and titrated against standard Pavy's solution. The result is expressed as grams of invert-sugar per 100 c.c. of the juice. The amount of cane-sugar (x) in 100 c.c. of the juice can be calculated from the formula $x = 0.95 (b—a)$ where a and b are the amounts of invert sugar in 100 c.c. of the sample before and after inversion respectively.

Total acid.

20 c.c. of the sample were heated rapidly to incipient boiling and quickly titrated against N/10 NaOH using litmus paper as indicator. The result is expressed in terms of tartaric acid. One c.c. of N/10 NaOH solution is equivalent to 0.0075 gram of tartaric acid.

Volatile acid.

20 c.c. of the sample were evaporated on a water-bath, till about 3 c.c. were left behind. About 20 c.c. of hot water were added and the solution was again evaporated to about 3 c.c. After repeating the process once more, the residue was diluted and titrated against N/10 NaOH. The result, expressed in terms of tartaric acid, gives the amount of fixed acid in the sample. The difference between the total acid and the fixed acid gives the amount of volatile acid which can be calculated in terms of acetic acid. One c.c. N/10 NaOH is equivalent to 0.006 gram of acetic acid.

Alcohol.

100 c.c. of the sample were exactly neutralised with sodium hydroxide solution, transferred to a distilling flask, and distilled till the distillate was about 80 c.c. A small quantity of tannin was added to prevent frothing. The distillate was made up to 100 c.c. and its alcoholic content determined with the help of an immersion refractometer.

Total extract.

50 c.c. of the juice were taken in a flat-bottomed platinum dish and evaporated to a syrupy consistency on a water-bath. The residue was heated for 3 to 4 hours in a drying oven at 100°, cooled in a dessicator and weighed.

Glycerol.

The procedure adopted was the same as that given on page 362 (5) of the Official and tentative methods of analysis of the Association of Agricultural Chemists (2nd edition).

Ash.

The weighed residue obtained in the estimation of extract was continuously charred at a low heat not exceeding dull redness, until it was free from carbon, and weighed.

Phosphorus Pentoxide.

50 c.c. of the sample were evaporated in a dish with 1 gram of a mixture of nitre (1 part) and Na_2CO_3 (3 parts). The residue was charred, washed with dilute nitric acid and filtered. The residue, after being washed with water on a filter paper, was thoroughly dried and incinerated in the original dish. The ash was moistened with HNO_3, taken up in boiling water and filtered. The filter paper and dish were washed several times with hot water. The first and the second filtrate together with the washings were collected in a beaker and evaporated to 10 c.c. When the temperature of the solution had fallen to about 50° C., 50 c.c. of the ammonium molybdate solution, prepared as described below, were added. After some time, 7 to 8 grams of ammonium nitrate were added and the liquid stirred to dissolve the salt and heated for about an hour at 45° to 50°C. The precipitate, thus obtained, was filtered through a Gooch crucible charged with asbestos, and washed with water acidified with 1 per cent. HNO_3, until a drop of the filtrate left no residue when evaporated on a watch glass. The crucible was then heated in an oven at 70 to 80°C., to constant weight. The ammonium molybdate solution was prepared as follows :—

40 grams of powdered ammonium molybdate were dissolved in a mixture of 320 c.c. of water and 80 c.c. of 20 per cent. ammonia, and the solution poured into a cold mixture of 480 c.c. of 30 per cent. HNO_3 and 170 c.c. of water. The reagent was kept in the dark for some days before use.

Nitrogen.

50 c.c. of the sample were digested with 16 grams of Na_2SO_4 and 1 gram of $CuSO_4$ in Kjeldahl's flask and nitrogen estimated as usual. The result is expressed as percentage of protein by multiplying the amount of nitrogen in 100 c.c. of the sample by 6.25.

The amounts of sugar and other constituents in the fresh juice show a considerable variation, according to (1) the time of the year, (2) the nature of the tree (date palm or toddy palm, male or female tree), (3) the age of the tree, (4) the locality in which the plant grows, (5) weather conditions prevailing at the time of tapping, and (6) the method of tapping. The results of analysis carried out in this laboratory on a number of samples of juice tapped from different trees at different times reveal that the percentage of total sugar in the fresh juice from the toddy palms is, on the average, greater than that in the juice from the date palms. It is found to vary from 10 to 13 per cent. in the first case and 6 to 10 per cent. in the second case. It is further found that the percentage of total sugar in the juice is, in general, greater in the dry season

(January to April) than in the rainy season (June to September). The ratio of cane-sugar to reducing sugars in the fresh juice is, on the average, 5 : 1. The results of two of the many analyses are given below :—

TABLE I

Analysis of the fresh juice from date palm (in grams per 100 *c.c.).*

1.	Total sugar expressed as invert sugar		9.52
	Cane-sugar	7.99	
	Reducing sugar expressed as invert sugar	1.49	
2.	Total acid expressed as tartaric acid		0.117
	Volatile acid expressed as acetic acid	.028	
	Fixed acid expressed as tartaric acid	.082	
3.	Alcohol		0.18
4.	Extract		9.880
5.	Glycerol		0.253
6.	Nitrogen		0.033
7.	Phosphate ($P_2 O_5$)		0.0508
8.	Ash		0.178

TABLE II

Analysis of the fresh juice from toddy palm (in grams per 100 *c.c.).*

1.	Total sugar expressed as invert sugar		10.1
	Cane-sugar	8.68	
	Reducing sugar expressed as invert sugar	0.96	
2.	Total acid expressed as tartaric acid		0.113
	Volatile acid expressed as acetic acid	0.036	
	Fixed acid expressed as tartaric acid	0.068	
3.	Alcohol		0.21
4.	Extract		10.53
5.	Glycerol		0.27
6.	Nitrogen		0.037
7.	Phosphate		0.048
8.	Ash		0.182

B.—Analysis of the fermented juice.

In addition to the constituents present in the fresh juice, the following were tested for and found present in the fermented juice :—

1. *Butyric acid.* The steam distillate was neutralised and evaporated to dryness on a steam-bath. The residue on being treated with a few c.c. of 10 per cent. sulphuric acid evolved the characteristic odour of butyric acid.

2. *Lactic acid.* The filtered sample was evaporated on a steam-bath to a paste and extracted three times with water-saturated ether. After distilling off the ether, the aqueous solution was tested with Uffelman's reagent prepared by mixing 10 c.c. of a 4 per cent. solution of phenol with 20 c.c. of water and adding one drop of a solution of ferric chloride. The clear amethyst colour of the reagent was turned yellow. The aqueous extract was also tested as follows : – A few drops of the solution were added to 5 c.c. of sulphuric acid in a test-tube, to which a drop of a saturated solution of calcium sulphate had previously been added. The tube was heated on a water-bath for 2 minutes. On cooling 2 to 3 drops of a solution of thiophene in alcohol (10 to 50 drops in 100 c.c. of alcohol) were added and the tube again heated on a water-bath. The solution became cherry-red in colour.

Lactic acid bacteria were also visible under the microscope.

The juice was allowed to ferment in a glass container at 20 to 25° and analysed during the course of fermentation. The quantities of the various constituents present in the juice on the 10th day of fermentation are given below :—

TABLE III

Analysis of the fermented palm juice after 9 days of fermentation (in grams per 100 *c.c.).*

1.	Total sugar expressed as invert sugar ..		.. 0.55
	Cane-sugar ..	..0.36	
	Reducing sugar ..	..0.17	
2.	Total acid expressed as tartaric acid ..		.. 0.943
	Volatile acid expressed as acetic acid ..	..0.460	
	Fixed acid expressed as tartaric acid	..0.368	
3.	Alcohol		.. 3.61
4.	Glycerol		.. 0.331
5.	Nitrogen		.. 0.123
6.	Phosphate		.. 0.051
7.	Ash		.. 0.196

C.—Changes in the Sugar, Alcohol and Acid Contents of the Juice during the course of Fermentation.

Many samples of juice, collected in disinfected glass vessels, were allowed to ferment under natural conditions, at a temperature ranging between 20 to 25° and analysed day by day with regard to their sugar, alcohol and acid contents. The results of this analysis, carried out with one sample which may be taken as an average sample, are given below :—

TABLE IV

Changes in sugar, acid and alcohol contents with fermentation (in grams per 100 *c.c.)*

Day	SUGAR			ACID			Alcohol
	Total sugar	Cane-sugar	Reducing sugar	Total acid in grams of tartaric acid	Fixed acid in grams of tartaric acid	Volatile acid in grams of acetic acid	
1st day ..	9.8	7.90	1.48	0.195	0.060	0.108	**0.26**
2nd ,, ..	5.5	3.12	2.21	0.338	0.162	0.140	**2.7**
3rd ,, ..	3.6	1.52	2.00	0.401	0.198	0.162	**3.2**
4th ,, ..	2.3	0.95	1.30	0.416	0.191	0.180	**4.0**
5th ,, ..	1.3	0.59	0.68	0.442	0.202	0.192	**4.0**
6th ,, ..	0.98	0.42	0.54	0.442	0.198	0.195	**4.1**
7th ,, ..	0.59	0.218	0.37	0.495	0.195	0.240	**4.3**
8th ,, ..	0.50	0.16	0.33	0.543	0.213	0.264	**4.4**
9th ,, ..	0.44	0.14	0.29	0.571	0.219	0.280	**3.9**
10th ,, ..	0.31	0.08	0.22	0.645	0.225	0.336	**3.8**

These results indicate that alcohol reaches its maximum concentration of 4.4 grams in 100 c.c. on the 8th day of fermentation, after which it gradually decreases, through acetic fermentation, which is rather a slow process under the prevailing conditions.

Our thanks are due to Mr. Naseem Mirza, M. SC. who helped us in a part of the work and to the authorities of the Excise Department for their very helpful co-operation.

A PRELIMINARY NOTE ON A COLLECTION OF SCORPIONS* FROM HYDERABAD (DECCAN), TOGETHER WITH SOME REMARKS ON THEIR VENOMS

BY

M. Rahimullah

(*With one Plate*)

During the course of several months I have been able to collect a large number of scorpions from different localities of Hyderabad, and some specimens were also sent to me by many of my friends from the various districts within the Hyderabad State.

Below I just intend to give some notes on certain diagnostic characters of these scorpions. In all, I have worked out five different species, belonging to two genera, *viz.*, ***Buthus*** and ***Palamnœus*** (falling under the families Buthidæ and Scorpionidæ respectively) :

(A) THE DIAGNOSTIC CHARACTERS OF THE FAMILY BUTHIDÆ AND OF THE GENUS *Buthus* :

Sternum almost invariably triangular narrowed in front ; 3rd and 4th legs usually furnished with tibial spurs. Fam. Buthidæ.

Abdominal terga with three crests ; all the caudal segments keeled.

Immovable finger of the mandible with two teeth below ; carapace with conspicuous keels . Genus Buthus.

(B) THE DIAGNOSTIC CHARACTERS OF THE FAMILY SCORPIONIDÆ AND OF THE GENUS *Palamnœus* :

Distal lateral edges of tarsi produced into a rounded lobe overlapping the base of claws and forming a very acute angle with the base of the claw lobe ; body and chelæ not flat ; hand without strong finger-keel ; tail strong, not compressed. Fam. Scorpionidæ.

FOOT-NOTE : – *A portion of this paper was read by the author before the Zoology Section at the 24th annual meeting of the Indian Science Congress, held at Hyderabad (Deccan) in January, 1937.

Carapace deeply notched in the middle line. Tarsal lobes of 3rd and 4th legs with 2, very rarely 3 spines. Brachium of Chelæ not or scarcely keeled, and furnished with only a few setiferous pores. Genus *Palamnæus.*

(C) DESCRIPTION OF THE SPECIES BELONGING TO THE GENUS *Buthus.*

(1) *Buthus tamulus*, Fabr. (Pl. fig. 2).

(*a*) *General characters :*

Colour : yellowish-brown, legs and vesicle usually yellow ; ocular tubercle and keels on the carapace black ; keels on terga and adjacent tubercles black ; tail reddish-yellow, its inferior and lateral keels black.

Carapace : scarcely as long as the 5th caudal segment, its keels granular. *Terga* with 3 keels, keels granular ; the keels of the last tergum granular and strong. *Sterna* smooth with the exception of keels which are usually granular.

Tail : intercarinal spaces granular, keels granular ; *vesicle :* large, granular below, as high as wide.

Chelæ : humerus with granular crests above ; brachium, hand and digits thickly hairy and without crest ; digits long and movable.

(*b*) *Measurements in m.m.*

♂ Total length 63, carapace 7.2, tail 40, brachium 7.2, underhand 5, movable finger, 8, width of hand 3.

Pectinal teeth=31.

♀ Total length 71.5, carapace 8, tail 43.5, brachium 8, underhand 5, movable finger 10, width of hand 10.

Pectinal teeth=28.

It is the commonest species to be found here, and is usually met with inside the houses too, where it even climbs up the doors, almirahs and other places.

(2) *Buthus pachyurus*, Pocock. (Pl. fig. 4).

(*a*) *General characters :*

Colour: uniformly black; hand and fingers, and extremities of legs reddish-brown.

Carapace : upper surface covered with coarse granules. *Terga :* upper surface entirely covered with coarse granules, amongst which the normal keels stand out as granular ridges. *Sterna :* smooth, irregular granules on the 5th.

Tail : coarsely granuler below, and also at the sides and upper surface. Segments 1, 2 and 3 wider than long, 4th nearly square. *Vesicle :* unfortunately I got the vesicle broken in this specimen. Tail about four times as long as the carapace.

Chelæ : no granules ; furnished with about 11 rows of teeth.

Legs : finely granuler.

(*b*) *Measurements in m.m.*

* ♂ Total length 38, carapace 6, tail 21 app., brachium 5, underhand 4, movable finger 5.

Pectinal teeth=22.

No ♀ was available. This species is not commonly found here.

(D) DESCRIPTION OF THE SPECIES BELONGING TO THE GENUS *Palamnæus*.

(1) *Palamnæus swammerdami*, Simon (Pl. fig. 3).

(*a*) *General characters :*

Colour : blackish or blackish-purple ; vesicle reddish-yellow ; hand and legs deeply reddish-brown.

Carapace : more or less covered with coarse granules, its lateral margins strongly converging in front. *Terga :* granular at the sides and posteriorly. *Sterna :* smooth and shining.

Tail : about 4½ times as long as the carapace ; all its segments coarsely granular above ; *Vesicle :* large with four rows of granules below.

Chelæ · humerus coarsely granular above and at the base below ; brachium rugose though scarcely definitely granular behind. Legs with granular femora ; tarsi armed beneath with 6 posterior and 4 anterior spines ; bristles on the tips of the lobes.

(*b*) *Measurements in m.m.*

♀ Total length 132, carapace 18, tail 89, brachium 15, width of hand 16, underhand 11, movable finger 17.

Pectinal teeth=19.

♀ Total length 151, carapace 21, tail 92, brachium 17, width of hand 19, underhand 13, movable finger 21.

Pectinal teeth=16-17.

It is the largest species of scorpion found in Hyderabad. and is commonly met with under boulders of stones. Very big ones are especially found in the districts of Raichur and Gulbarga, where the people call them " *Chappal bitchchu* " (or the so-called " sole-scorpion "), because of their huge size, and more or less flattened form. Pocock reports the largest specimen to be about 179 m.m., and he says that it is the largest species of scorpions found in India.

FOOT-NOTE :—In addition, *Buthus acute-carinus* has been previously reported from this locality. Cf. Rahimullah and Das Journ. Osm. Univ. Coll., Vol. I, 1933.

*Aculeus was broken in this specimen.

(2) *Palamnœus fulvipes*, C. Koch. (Pl. fig. 1).

(*a*) *General Characters :*

Colour : uniformly blackish on the dorsal side; vesicle reddish-yellow; tail yellowish-brown; legs reddish-yellow; hand blackish-brown; underside lighter in colour and blackish-brown.

Carapace : much flatter and not swollen in the middle, finely granular at the sides and in front, longer than every caudal segment, its sides not abruptly converging in front. *Terga :* granular at the sides, smooth in the middle. *Sterna :* smooth.

Tail : about 3 times as long as the carapace; *vesicle :* granular below, and at the sides.

Chelæ : brachium granular, hand tuberculate on the dorsal side and feebly so on the ventral; inner surface of the hand convex.

Legs : as in *P. swammerdami.*

(*b*) *Measurements in m.m.*

♂ Total length 76, carapace 13, tail 46, brachium 10, underhand 9, movable finger 12, width of hand 11.

Pectinal teeth = 14-16.

♀ Total length 80, carapace 14, tail 40, brachium 9, underhand 8, movable finger 12, width of hand 11.

Pectinal teeth = 12-13.

It is the commonest species of *Palamnœus* found in Hyderabad, and is generally seen in damp places, and sometimes in houses too.

(3) *Palamnœus xanthopus*, Pocock. (Pl. fig. 5).

(*a*) *General Characters :*

Colour : carapace yellowish-brown; dorsal surface dark-brown; tail reddish-yellow; vesicle yellow; underside and legs yellowish; tips of chelæ brownish-red.

Carapace : weakly granular laterally, longer than 3rd and 4th caudal segments. *Terga :* smooth. *Sterna :* smooth, the last with 4 crests.

Tail : about 3 times as long as the carapace, feebly granular laterally, 5th segment carinate; *Vesicle :* granular at the sides.

Chelæ : brachium with superior crest granular, hand not crested above. Spines on tarsi 4-5.

(*b*) *Measurements in m.m.*

♀ Total length 64, carapace 12, tail 35, brachium 8, underhand 7, movable finger 11, width of hand 9.

Pectinal teeth = 13.

No males of this species were found in the collection. It is an uncommon species in Hyderabad.

(E) REMARKS ON THE TOXICITY OF SCORPION VENOMS.

I may mention here certain views on the venoms of scorpions. Regarding the toxicity of the scorpions, S. H. Prater, in 1929, says : " The small red scorpions of the genus *Buthus* are known to be far more virulent than are the large black rock scorpions (*viz.*, *Palamnœus*), though the latter look very much more deadly and forbidding ; while the dose of poison given by such a species as *B. australis* is, of course, definitely smaller, its toxicity is comparable in virulence to that of the cobra." It may be presumed that this is evidently an exaggerated statement of facts.

Father Caius, formerly a biochemist of the Haffkine Institute, Bombay, since 1912, had been carrying on some very interesting work and experiments on the toxicity of the poison of scorpions, and he says that the quantity of venom obtained from a scorpion is at the most 12.6 milligrammes.

In the editorial section of the Journ. Bombay Nat. Hist. Soc., Vol. 33, No. 2. p. 413, 1929, Prater mentions at great length the work of Caius regarding the toxicity of the venom of scorpions. He says that two deaths were reported from the Central Provinces owing to the stinging of scorpions, and it was thought desirable to investigate the matter thoroughly, because the common belief was that the sting of a scorpion is fatal only to very weak individuals and children below 7 years of age. In the two cases reported from Raipur and Drug (Central Provinces) it was found that the victims were two male healthy children of 9 and 11 years of age respectively and in both the cases the scorpions were *B. hendersoni*, Pocock. Of course, it is quite possible that there may be many similar reports from other parts of India too, though unrecorded.

In the same editorial, Prater further says, (p. 414) " That the toxicity of the venom may also vary in the same species, this being dependent on the conditions of secretion. The first drop of venom given out by a scorpion is far more potent than succeeding drops. It has been proved by experiment that the venom contained in the duct is far more virulent than that which is secreted in the gland itself. The venom found in the duct is a more elaborate product. It is believed to be the result of the maturation of the poison secreted in the gland. When mature venom is exhausted, the supply which follows immediately loses much of its toxic properties."

It would be interesting to quote some lines about the Arizona scorpions by Stahnke as follows :—

> " More lives have been lost in Arizona from the sting of the scorpion than from the bite or sting of any other venomous arthropod or reptile at least during

the nine year period since 1929. For a period of six and one half years, beginning with 1929, there were recorded twenty-five deaths resulting from the sting of the scorpion and only ten deaths caused by the rattle-snake, gila monster and other poisonous animals. Most of the deaths due to scorpion sting have occurred in the Southern parts of the State, particularly in the Salt River Valley, and the victims have been children usually six years of age and under. The writer knows of one case in which an eight-year old child succumbed to a scorpion sting."

In this article he has narrated the effect of poison on white rats and also his experience on children. He also mentions the results of anti-scorpion serum on rats stung by *Centruroides sculpturatus* Ewing, and found it to be effective, even though the animals were in advanced stages of poisoning. He says that since then the serum has been tried on human victims of *C. sculpturatus*. In all cases it has proved entirely effective, and no deaths have resulted from scorpion sting, even though the serum was used in quite later stages of poisoning.

I am much indebted to Professor M. Qureshi for his kindly accepting this paper for publication. I am much thankful to Dr. F. H. Gravely, Superintendent of the Government Museum, Madras, for the help given to me in the identification of these scorpions. I am also thankful to Professor B. K. Das of this Department for his constant help, guidance and encouragement throughout my work.

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DESCRIPTION OF THE PLATE

A PHOTOGRAPH OF THE FIVE SPECIES OF SCORPIONS.

(*Dorsal aspect* ×2/3 *circ.*)

Fig. 1	*Palamnæus fulvipes*, C. Koch.
Fig. 2.	*Buthus tamulus*, Fabr.
Fig. 3.	*Palamnæus swammerdami*, Simon.
Fig. 4.	*Buthus pachyurus*, Pocock.
Fig. 5.	*Palamnæus xanthopus*, Pocock.

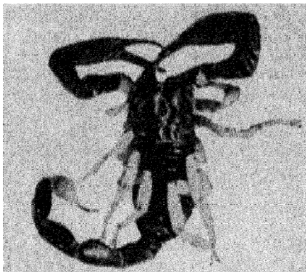
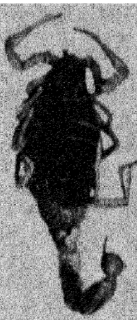


Fig. 1.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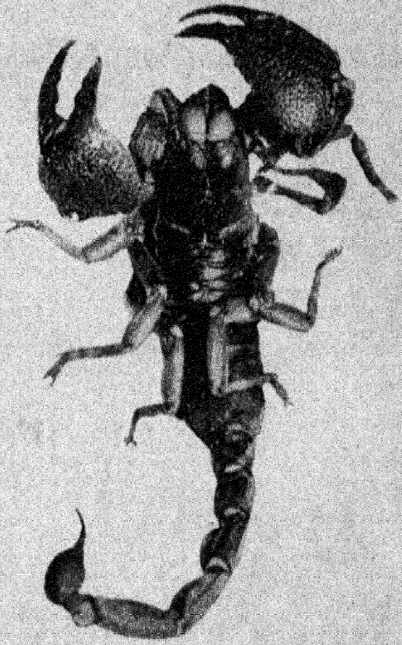
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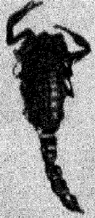
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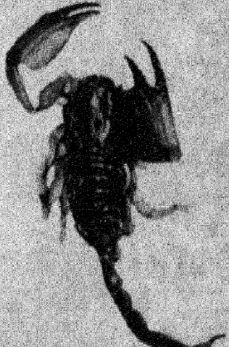
Fig. 5.